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Measurement of Triplet Optical Densities of Organic Compounds by Means of CW Laser Excitation

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Measurement of Triplet Optical Densities of
Organic Compounds by Means of CW Laser Excitation ·

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ABSTRACT

The application of cw lasers as powerful excitation sources for transient (triplet-) state spectroscopy is demonstrated. By focusing a cw laser beam on a sample with the aid of a lens, high triplet optical densities $OD_T(\lambda)$ can be recorded. Using McClure's method, triplet extinction coefficients $\epsilon_T(\lambda)$ of many organic compounds are conveniently measured. To illustrate the method, we recorded ϵ_T values on syn-(dimethoxyphosphinylmethyl,methyl) bimane. Exciting organic compounds with light causes various degrees of photodecomposition. We have developed a method to measure triplet optical densities $OD_T(\lambda)$ in the presence of photodecomposition. The method is demonstrated on Coumarin 120. One records $OD_T(\lambda)$ values as well as the accumulation of absorbing photoproducts as a function of time. Turning off the cw laser excitation, one records the accumulation of photoproducts only. Separating the two processes, one can determine how the triplet optical density declines as a function of time t. The decline curve can be expressed with an equation that is of second order in time. This equation allows one to extrapolate back to $t = 0$ and recover OD_T when there was no photodecomposition. Because the cw laser light is highly polarized, triplet-triplet (T-T) photoselection spectroscopy can be employed. The degree of polarization P of several syn-binanes was recorded, providing important insight on the polarization of T-T transitions. These data may be used to improve laser action properties of syn-bimanes by substitutions.

INTRODUCTION

The UV/visible/near-IR absorption spectra of organic compounds are among the most widely studied. These spectra result from the excitation (absorption) of light. Molecules are excited from the (singlet) ground state into higher singlet states,

$$N_S + h\nu_A \rightarrow N_S^*, \text{ or } N_S^{**}, N_S^{***}, etc. \tag{1}$$
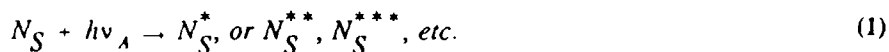
If excited into the N_S^{**}, N_S^{***}, etc., states, the molecules relax radiationless to N_S^*. From N_S^*, the molecule can undergo four different decay processes,

$$N_S^* \rightarrow products \tag{2}$$

$$N_S^* \rightarrow N_T + heat \tag{3}$$

$$N_S^* \rightarrow N_S + heat \tag{4}$$

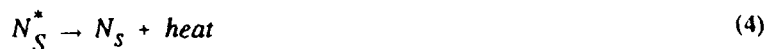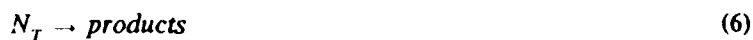$$N_S^* \rightarrow N_S + h\nu_F. \tag{5}$$

Fig. 1 presents the different paths of decays possible. Molecules in the triplet state can undergo transitions similar to those possible in the singlet state; i.e.,

$$N_T \rightarrow products \tag{6}$$

$$N_T \rightarrow N_S + heat \tag{7}$$

$$N_T \rightarrow N_S + h\nu_P . \tag{8}$$

Significantly, in the presence of radiation of proper wavelength, the molecules in the triplet ground state N_T can be excited into higher triplet states,

$$N_T + h\nu_T \rightarrow N_T^*, N_T^{**}, etc. \tag{9}$$

This process is called triplet-triplet (T-T) absorption and is the subject of this presentation. There is only limited experimental data available on the T-T absorption spectra of organic compounds.

The first T-T absorption spectrum was observed in 1941 by Lewis, Lipkin, and Mangle. They discovered a transient absorption spectrum of fluoresceine dissolved in boric acid. This spectrum is only observable during intense illumination [1].

In a 1984 compilation of triplet optical densities OD_T and triplet extinction coefficients ϵ_T by Carmichael and Hug [2], they list only 1,143 organic compounds. These data were obtained by using different measurement methods and excitation sources. The data are of various measurement accuracies and, indeed, contain moderate to considerable measurement errors.

As in conventional absorption spectroscopy, triplet (and other excited or metastable) optical densities OD_T are defined by the Lambert-Beer law,

$$OD_T(\lambda) = \log I_o/I = N_T \epsilon_T(\lambda) \, d . \tag{10}$$

d presents the thickness of the sample, I_o is the intensity of the probing (monitoring) light with excitation off, and I the light with excitation on. The experimental difficulties in excited-state spectroscopy are (a) the generation of a sufficiently large and (b) the determination of the concentration of the excited (triplet) molecules N_T.

To generate triplet-state molecules N_T, both pulsed (flashlamp and lasers) and steady-state (high-pressure Hg/Xe arc lamp and cw lasers) are used for excitation. Pulsed excitation is most useful for obtaining kinetic data on the organic molecules present in the gas phase or solutions. For obtaining OD_T and ϵ_T values, the steady-state method is experimentally more convenient. The compound is dissolved in a solid, generally in a glassy solvent. In solids, the triplet-state lifetime τ_T is much prolonged, resulting in increased concentrations of triplet-state molecules N_T. Very large concentrations of triplet-state molecules are obtained when cw lasers are employed as excitation sources [3,4]. Therefore, using the steady-state method together with cw laser excitation, triplet extinction coefficients ϵ_T as well as polarization data on T-T transitions can be obtained on a very large number of organic compounds, including compounds having triplet-state lifetimes τ_T down to about 10^{-3} s [5].

The intensities of the monitoring light I and I_o are conveniently recorded with the aid of a strip-chart recorder. Measuring triplet optical densities is important for the following reasons:

1. Triplet-state molecules play a major role in photochemistry. Having the ϵ_T values of the reacting triplet-state species available allows one to determine their concentrations N_T. These data then can be used to obtain information on the rate equations involved in the photochemical reaction.

2. T-T absorption spectra (OD_T values) plus the degree of polarization P provide information on the energy and symmetry of higher triplet states. This, in turn, allows one to check the consistency of quantum mechanical calculations.

3. The negative effect of triplet-state molecules generated during excitation on the efficiency and photostability of organic dyes used as active media in dye lasers is well known. As examples of organic compounds, we use laser dyes in this presentation. It is our opinion that the efficiency as well as the photostability of laser dyes can be improved by employing the experimental methods outlined in this presentation of how to measure triplet optical densities conveniently to obtain guidelines on chromophores as well as substituent selection for laser dye synthesis.

EXPERIMENTAL

1. Spectroscopic Equipment and Procedures

The experimental layout is shown in Fig. 2 [5]. The sample S, which contains the organic compound dissolved in a glassy solvent, is submerged in liquid nitrogen. The sample is excited with the cw laser. The laser light is focused on the sample with the aid of lens L_3. Laser lines are selected for excitation depending on the intensity of the absorption spectrum of the compound to be studied. The power meter can be moved in and out of the laser beam path to record its intensity (power) I_{ex}. The light from the monitoring light source MLS, after being focused on the pinhole PH, is chopped and phase-sensitive detection is used. This allows one to discriminate against scattered laser light, fluorescence, and phosphorescence emitted by the sample. The small excitation area, which contains the high concentration of triplet-state molecules N_T, is exactly focused with the aid of lens L_4 on the small hole in the dovetail blade, which is positioned in front of the monochromator slit (SL).

The sample, a quartz cell that had a diameter of 5/8 inch and a thickness d = 3 mm, contained the glassy solution. It was submerged in a liquid nitrogen dewar that had flat, 1-inch-diameter quartz windows as shown in Fig. 2. When experiments with photosensitive compounds were performed, the liquid nitrogen dewar was mounted on an Aerotech vertical assembly #AVA-9, which allowed the dewar and the sample to be lifted to make a sample area available that had not previously been exposed to excitation.

The experiments consisted mainly of measuring intensities of the monitoring light passing through the sample and applying Lambert-Beer's law. I_o presents the light intensity before excitation and I the intensity during excitation. If corrections were made for photodecomposition, the intensity of the monitoring light after excitation, I_o', was also recorded.

The success of the performed experiments (that is, the production and measurement of high triplet optical densities) requires that the small excitation area be focused exactly on the small hole in the dovetail plate in front of the monochromator slit. This can be accomplished by either focusing the small fluorescence (excitation) area directly on the small hole, or by moving the lens L_3, which is focusing the cw laser excitation light on the sample, perpendicularly (up/down, left/right) to the laser beam until one observes minimum monitoring light intensity I (maximum T-T absorption) on the strip-chart recorder.

2. Measuring Triplet Extinction Coefficients by McClure's Method

Carmichael and Hug in their review article [2] list seven different methods to measure triplet extinction coefficients ϵ_T of organic compounds. Among them, the intensity variation method proposed by McClure [6]. This method, together with cw laser excitation [3,5], appears to us to be the most simple as well as the most accurate one [7]. Besides the concentration N_S of the compound, only the thickness of the sample d has to be known. One simply inserts the power meter PM into the light beam and measures the power (intensity) I_{ex} of the cw laser beam. However, one needs only relative values, and it is only necessary to determine optical density values OD_T at different intensities I_{ex}. When using McClure's equation

$$1/OD_T = (1/N_S \epsilon_T d)(1 + A_i/I_{ex}) \tag{11}$$

with A_i = kinetic constants, one plots $1/OD_T$ versus $1/I_{ex}$ and extrapolates to the ordinate for $1/I_{ex}$ = 0 (or $I_{ex} = \infty$), to obtain $1/OD_T^\infty$. Thus $OD_T^\infty = N_S \epsilon_T d$ and $N_S = N_T$. At infinite excitation intensity (power) I_{ex}, all molecules would have been converted into their triplet state. Because Eq. (11) is a linear relationship, only two values of OD_T need be determined at two different I_{ex} powers to extrapolate to $1/OD_T^\infty$. However, measuring more than two $1/OD_T$ values should increase measurement accuracy.

3. Triplet-Triplet Photoselection Spectroscopy

To obtain polarization data on T-T absorption spectra of organic compounds, an analyzer A is inserted between the lenses L_2. The analyzer can be either positioned parallel (∥) or perpendicular (⊥) relative to the polarization of the cw laser beam. One needs four measurements ($I_0^\parallel$, $I^\parallel$, $I_0^\perp$, $I^\perp$) to record the degree of polarization P:

$$P = \frac{OD_T^\parallel - OD_T^\perp}{OD_T^\parallel + OD_T^\perp} = \frac{\epsilon_T^\parallel - \epsilon_T^\perp}{\epsilon_T^\parallel + \epsilon_T^\perp} = \frac{3\cos^2\theta - 1}{\cos^2\theta + 3} \tag{12}$$

with $OD_T^\parallel \equiv \log I_0^\parallel/I^\parallel = N_T \epsilon_T^\parallel d$ and $OD_T^\perp \equiv \log I_0^\perp/I^\perp$. When the absorbing singlet and triplet dipoles are parallel to each other ($\theta = 0°$), one obtains P = 1/2; if they are perpendicular to each other ($\theta = 90°$), P = -1/3. However, experimentally, P in terms of exactly 1/2 or -1/3 are rarely observed.

Absolute polarization measurements [that is, the determination of the direction of an electronic dipole (the transition moment) within an organic molecule] are difficult to obtain experimentally. For example, if one would like to measure the direction of a singlet-singlet (S-S) dipole that is responsible for the S-S absorption of the molecule, the following procedure is generally used. The compound has to be dissolved in a host crystal and its geometrical arrangement relative to the host crystal must be known. This information is obtained with the aid of x-ray crystallography. The S-S absorption of the host crystal must be at much shorter wavelengths than that of the molecule studied. No polarization data can be obtained beyond the onset of the absorption in the host crystal. This is probably the most difficult requirement. Often, guest and host crystals are not compatible with each other; i.e., the guest molecule cannot be dissolved in appreciable concentration in the host crystal.

Contrary to the absolute determination of the direction of a dipole within a molecule, photoselection spectroscopy is experimentally rather simple. One fixes the guest molecule within the solute by dissolving it in an organic solvent (glassy solvent) that forms a glass at liquid nitrogen temperature. If one excites the sample with polarized light (from a laser, for example), one generates a crystal-like arrangement of excited guest molecules within the glass solvent. Only guest molecules that have their absorbing electronic dipole(s) arranged parallel to the electric vector of the polarized light will be excited.

Therefore, photoselection spectroscopy provides data on the orientation of the absorbing (S-S) electronic dipole relative (angle θ) to the fluorescence, phosphorescence, or T-T dipoles [8]. In a symmetric molecule, these dipoles are positioned either along the short or long molecular axis. For example, recording a degree of polarization of P = 0.4 does not provide any information on the absolute orientation of the dipoles within the molecule, but only that the two dipoles are aligned parallel with each other. Applying photoselection spectroscopy to T-T absorption studies, a change of P with wavelengths indicates the presence of a different T-T transition. Therefore, photoselection spectroscopy is important in assigning or finding new electronic transitions. We present T-T polarization spectra and their interpretation of some syn-bimanes.

## TRIPLET EXTINCTION COEFFICIENT OF SYN-(DIMETHOXYPHOSPHINYLMETHYL,METHYL) BIMANE

The terms syn-dioxabimanes and syn-(R_2,R_1) bimanes are the trivial names for 1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-diones, a recently developed family of compounds that have many interesting chemical [9-14] and spectroscopic [15-18] properties. A strong fluorescence, generally characteristic of the syn-bimanes, but not of the anti-bimanes, is subject to large solvatochromic effects. The compound syn-(methyl,methyl) bimane, for example, shows strong fluorescence, its

intensity maximum shifting from 420 to 460 to 480 nm as one changes from p-dioxane to ethanol to water as solvents. A T-T absorption band with maximum intensity at 480 nm declines in intensity rather steeply towards longer wavelengths, but less steeply towards shorter wavelengths.

Laser action was observed for many syn-bimanes that possess high quantum fluorescence yields ($Q_F > 0.7$) [19-21]. Laser action under flashlamp excitation is generally observed in the 505- to 515-nm spectral region with water or fluorinated alcohols as solvents. These are the solvents that cause the largest red shifts. No profound solvent effect on the T-T absorption band at 480 nm of syn-(methyl,chloro)bimane was observed [20]. Laser action can also be observed in the 435-nm spectral region from the same compound, as shown in Fig. 3, when p-dioxane is used as a solvent [21]. This is the solvent that caused the smallest red shift. Because of the overlap with considerable T-T absorption in the 505- to 515-nm, as well as in the 435-nm spectral region, laser action in the syn-bimanes is not very efficient. To improve laser-action efficiency in the syn-bimanes, one would like to find proper substituents in the R_1 and/or R_2 positions to red shift only the T-T absorption spectrum in Fig. 4 only or to red shift the S-S together with the fluorescence spectrum only to have the fluorescence (laser action) spectral region fall into a spectral region of low T-T absorption.
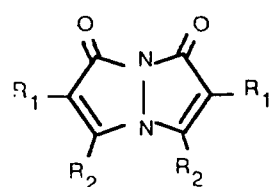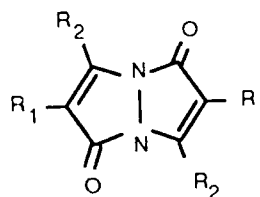
syn (R_2, R_1) bimane   anti-(R_2, R_1) bimane

After recording OD_T values, one generally measures one ϵ_T value at a T-T absorption maximum. In Fig. 5, we show the extrapolation of the $1/OD_T^{\infty}$ of syn-(dimethoxyphosphinylmethyl,methyl) bimane. The concentration 1 and 2×10^{-4} (corrected for contraction) yields $\epsilon_T(480) = 2.52$ and 1.47×10^3 ℓ/mole cm, respectively. Only the first value is of significance, so the second has to be discarded. Because the measurements are performed at the temperature of liquid nitrogen, two facts have to be considered.

(a) Lowering the temperature, solubilities of compounds are reduced. Starting out with a certain concentration at room temperature, lowering the temperature to that of liquid nitrogen will often result in saturation, but with the saturation concentration unknown. Using the room temperature concentration N_S in $OD_T^{\infty} = N_S \epsilon_T$ d will yield a too-small value of ϵ_T. The saturation concentration is smaller than the room-temperature concentration N_S. However, performing measurements on solutions of different concentrations N_S, one obtains a smaller ϵ_T value at the higher concentration, in the presence of saturation [7].

(b) Cooling the sample down to the temperature of liquid nitrogen causes the solution to contract, yielding concentrations that are higher than the ones present at room temperature. Therefore, the ϵ_T values obtained from the relation $OD_T^{\infty} = N_S \epsilon_T$ d have to be multiplied with a contraction factor ρ. This factor is 0.84 for 2-methyltetrahydrofuran.

McClure's method allows one to measure the triplet extinction methods of many organic compounds. The method is applicable to molecules with triplet-state lifetimes τ_T as small as 10^{-3} s [5-7, 22, 23]. However, the main difficulty in measuring the ϵ_T values of a very large percentage of compounds is photodecomposition. How to account for photo-decomposition will be discussed in the next section.

MEASURING TRIPLET OPTICAL DENSITIES IN THE PRESENCE OF PHOTODECOMPOSITION

Exciting organic compounds with light and depending on wavelength, intensity, and exposure time, one always observes moderate to considerable photodecomposition. We presented the different pathways of activation, deactivation and photodecomposition of organic compounds at the beginning of this presentation. When recording triplet optical

densities, only few compounds can be termed photochemically rather stable [7]. Most compounds show various degrees of photodecomposition, resulting in measurement errors. For a large percentage of compounds, one has simply to discard any attempt to obtain meaningful data on triplet optical densities OD_T over a wider spectral range.

Measuring triplet optical densities, the observed photodecomposition is actually the combination of two different effects. First, photodecomposition results in the reduction of concentration of N_T, and consequently of N_S. Owing to decomposition, a reduction of the triplet optical density is observed as a function of time. Second, photodecomposition results in the buildup of photoproducts with time. One can introduce a photoproduct optical density $OD_p = N_p \epsilon_p d$, with N_p the concentration of the photoproducts and ϵ_p the corresponding extinction coefficients of the products.

Although both OD_T and OD_p are measured simultaneously during excitation, after excitation OD_p only is measured. Significantly, this allows one to separate the two processes. If a mathematical expression for the decay of OD_T with time can be found after separating OD_p, one may be able to extrapolate back to t = 0, when $N_p(t=0) = 0$ and therefore N_T (i.e., OD_T) has not yet been reduced by photodecomposition.

Therefore, to correct for photodecomposition, the following procedure is used: After the time intervals t_1, t_2, etc., the excitation light is turned off and the corresponding $I(t_1)$, $I(t_2)$, etc., values are recorded. After each measurement, one waits until the intensity of the monitoring light has reached steady state, yielding I_o'. We then have $N_T = 0$. From these two values, the triplet optical density is calculated:

$$OD_T(t_n, \lambda) = \log I_o'(t_n, \lambda)/I(t_n, \lambda) - N_T(t_n) \, \epsilon_T(\lambda) \, d. \tag{13}$$

When there is no photodecomposition present, one has $I_o = I_o'$. With photodecomposition, one has $I_o > I_o'$. Using I_o' instead of I_o to calculate the OD_T values, one accounts for photodecomposition. This statement follows when one considers the Lambert-Beer law for a mixture of N_T and N_p.

$$I = I_{T+P} = I_o e^{-N_T \epsilon_T d - N_p \epsilon_p d} \tag{14}$$

$$I_o' = I_P = I_o e^{-N_p \epsilon_p d} \tag{15}$$

$$I_T = I_o e^{-N_T \epsilon_T d} \tag{16}$$

$$I = I_{T+P} = I_P e^{-N_T \epsilon_T d} = I_o' e^{-N_T \epsilon_T d} \tag{17}$$

$$\log I_P/I_{T+P} = \log I_o'/I = N_T \epsilon_T d \tag{18}$$

with I_{T+P} being the intensity of the monitoring light during excitation with triplet-state N_T and photoproduct molecules N_p present; I_p being the intensity on the monitoring light with excitation off and only photoproducts N_p present; and I_T being the intensity of the monitoring light with excitation on and only triplet-state molecules N_T present.

At a fixed wavelength, one may try the following expression for OD_T as function of time:

$$OD_T(t) = A_1 + A_2 t + A_3 t^2 \tag{19}$$

with $A_1 \equiv OD_T(t=0)$. Three measurements at times t_1, t_2, and t_3 are needed to obtain the constants A_1, A_2, and A_3.

We will present the determination of the $OD_T(t=0)$ and $\epsilon_T(\lambda)$ values of Coumarin 120 in some detail as an example of a strongly photochemically decomposing compound in the glassy solvent we employed.

ϵ_T values of Coumarin 120 are reported in [5]. In these experiments, a mixture of ethanol/methanol ratio 4:1 was used as a glassy solvent (ρ = 0.79). Under excitation with the argon ion lines at λ_{cw} = 351.1/363.8 nm, this compound was fairly stable photochemically. Using the estimation outlined in [7], the ϵ_T values reported should be accurate within ±25%. We switched to a mixture of n-butanol/iso-pentane ratio 3:7 as the glassy solution. Photodecomposition was much more severe than in the ethanol/methanol glassy solution. This allowed us to correct for photodecomposition and then compare the obtained ϵ_T value with that obtained in the ethanol/methanol mixture, which did not show strong photodecomposition.

Fig. 6 presents three typical $I(t,\lambda)$ curves, each measured at different wavelengths.

In curve A (λ = 580 nm), after turning on the excitation light, $I(t)$ passes through a minimum and then increases steadily; i.e., $OD_T(t)$ is steadily decreasing. Turning off the excitation light after 50 s, $I(t)$ exponentially reaches $I_0^!$, which comes rather close to the original I_0 value.

In curve B (λ = 480 nm), after turning on the excitation light, one reaches a pseudo steady state. Turning off the excitation light after 50 s, $I_0^!$ is somewhat smaller than I_0.

In case C (λ = 440 nm), after turning on the excitation light, $I(t)$ seems to decline steadily, apparently not reaching a steady-state value. After turning off the excitation light, $I_0^!$ is considerably smaller than the original I_0. However, $I(t)$ does reach a steady-state value after a considerable length of time. For $t \rightarrow \infty$, $N_T \rightarrow 0$ and one has $I(t) = I_0^!$; i.e., OD_T = 0.

Curves A, B, and C are typical curves and are always observed when photodecomposition is present. Even in cases for which apparently only small photodecomposition is present, curves A, B, and C are obtained by either prolonged excitation or by increasing the excitation intensity (power) I_{ex}. Curve C, where it appears that no steady state is present, might prompt one to discard the entire experiment.

Remembering, however, the presence of two opposite optical absorption mechanisms, namely the decline of T-T absorption owing to the reduction of N_T with time and an increase of absorption by photodecomposition products with time, curves A, B, and C can be explained easily. In curve A, one mainly observes the decline in T-T absorption owing to reduction of N_T and N_S, the original concentrations of the compound. After turning off the excitation light, $I_0^!$ returns almost to I_0, indicating weak absorption (small ϵ_p of the photodecomposition products. In curve C, the opposite is the case. There is small T-T absorption (small ϵ_T), but strong absorption (large ϵ_p) of the photodecomposition products. After considerable time, one does observe a steady state. This is the case when $N_S = N_P$ (and N_T = 0). Curve B is simply the case when the two opposite absorption mechanisms balance each other.

Obtaining $OD_T(t)$ values after time intervals t_1, t_2,...,t_n, and plotting the OD_T values as a function of t, one is able to obtain $OD_T(t=0)$ by using Eq. (10), where there is no photodecomposition present.

In Fig. 7, we present some $OD_T(t)$ values taken at different spectral regions of T-T absorption at t_1 = 15-, t_2 = 30-, and t_3 = 45-s intervals. The points do not fall on a straight line, but can be presented by the second-order Eq. (19).

It must be emphasized that t_1 must be larger than the time t_s needed to reach the steady state.

We used a pocket calculator to obtain the constants A_1, A_2, and A_3 and arrive at the curves obeying Eq. (10). These are presented in Fig. 7.

It appears that all the curves presented in Fig. 7 have the same minimum at some time t_m, which is given by dOD_T/dt = 0, $A_2 + 2 A_3 t_m$ = 0, where t_m is not a function of wavelength λ. A confirmation of this assumption has to wait until measurement accuracy has been improved.

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To obtain the ϵ_T values, we performed two runs each for the concentrations 1×10^{-4} and 2×10^{-4} molar at 580 nm. For each run, two OD_T values were recorded and their averages used. We calculated the averages from the two runs and present them in Fig. 8. We wanted to cover a rather wide range of I_{ex} values, namely from 1.43 to 10 mWatt cw laser power. As it is apparent from Fig. 8, at higher-power I_{ex} levels, there are deviations from the linear relationship (Eq. 11). Therefore, for the 1×10^{-4} molar solution we discarded the measurements at 10 mWatts (the point 0.1) and used all other six measurements. For the two runs, we obtained $\epsilon_T(580) = 8.6$ and 9.0×10^3 ℓ/mole cm (corrected for contraction). For the 2×10^{-4} molar solution, we used all seven measurements.

We obtained, for the two runs, $\epsilon_T(580) = 9.8$ and 10.0×10^3 ℓ/mole cm. The average for all four runs is $\epsilon_T(580) = 9.4 \times 10^3$ ℓ/mole cm. This value should be accurate within $\pm 25\%$, and agrees rather well with the 7.1×10^3-ℓ/mole cm value reported in [6], which was recorded with much reduced photodecomposition. This ϵ_T value should also be accurate within $\pm 25\%$, according to the error estimate given in [7].

Using the value of $\epsilon_T(580) = 9.4 \times 10^3$ ℓ/mole cm and the $OD_T(\lambda)$ values obtained from $\lambda = 420$ to 640 nm, we present the T-T absorption spectrum of Coumarin 120 in Fig. 9. In Table I, we present the $\epsilon_1(\lambda)$ values obtained in [5] with the values obtained in this work.

We also calculate the absorption spectrum ($OD_p \equiv \log I_o/I_o'$) of the photodecomposition products, using Eq. (16) and $t = 45$ s. These data also are presented in Fig. 9. It is apparent that the maximum intensity of absorption of the photoproducts, unfortunately overlaps strongly with the fluorescence (laser action) spectral region of Coumarin 120 centered at about 440 nm. This is a common observation on Coumarin laser dyes [24], which generally exhibit considerable photodecomposition.

In summary, we have presented a method to measure triplet optical densities $OD_1(\lambda)$ and triplet extinction coefficients $\epsilon_T(\lambda)$ of organic compounds in the presence of strong photodecomposition. The $\epsilon_1(\lambda)$ values obtained for Coumarin 120 agree well with those obtained when measured with considerable less photodecomposition.

To improve measurement accuracy, we suggest the following improvements:

1   Switch from the single-beam method (i.e., measuring I_o and I separately) to a two-beam method. All modern absorption spectrographs employ the two-beam method, in which I_o and I are recorded simultaneously. This would bring about considerable improvements in measurement accuracy and sensitivity in measuring the OD_T values.

2.   The requirement to lift the sample and dewar after alignment introduces measurement errors. A different experimental arrangement than the one used (see Fig. 2) might reduce these errors.

3.   Note that by using Eq. (19), one introduces a small error. At $t = 0$ when the sample is excited, one actually has $N_T = 0$ and therefore $OD_T = 0$. The buildup of N_T is exponential. Only after the steady state has been reached does Eq. (19) hold. Although the buildup of N_T is obscured by photodecomposition, the exponential decline of N_T after the excitation has been turned off is not. Therefore, from the decline of N_T after turning off the excitation light, one can measure the triplet decay constant, τ_T. One could include an exponential decay factor in Eq. (19) and start to make measurements even before the steady state has been reached. However, taking the decay constant into account can only be done after measurement accuracy has been improved.

POLARIZATION OF THE T-T ABSORPTION SPECTRA OF SOME SYN-BIMANES

According to Fig. 3 and 4, there is some overlap of the T-T absorption with the fluorescence (laser action) spectral region. From these figures, it is also apparent that there is a spectral region, starting at about 525 nm and extending to longer wavelengths, where diminishing T-T absorption is present. One would like to perform substitutions in the syn-bimanes, that shift the fluorescence spectrum to very low T-T absorption, to obtain efficient laser action.

Substitution with an electron donating (e.g., auxochromic) group will generally red shift all S-S and T-T absorption bands that have their originating electronic dipole positioned in the molecule in the direction of (or near) the substituent. Therefore, long-axis substitution will generally red shift all long-axis-polarized S-S and T-T absorption bands, and will leave all short-axis-polarized S-S and T-T bands more or less unaffected. Corresponding results are obtained for short-axis substitution. Often, substitution with an electron donating group will also intensify S-S and T-T absorption bands (hyperchromic effect).

The compound syn-(methyl,hydrogen) bimane was the simplest syn-bimane we studied. Some of its spectroscopic properties are reported in [20,25]. The T-T absorption, as well as S-S absorption and fluorescence spectrum, are shown in Fig. 10. This T-T absorption spectrum is very similar to other syn-bimanes, which do not contain any electron withdrawing or attracting substituents in the R_1 and R_2 positions. Noteworthy is the polarization spectrum P on top of the T-T absorption spectrum. Clearly, there are two differently polarized T-T transitions present. The shoulder at about 420 nm is not a vibrational progression of the T-T intensity maximum located at about 490 nm. The presence of two differently polarized, closely spaced T-T transitions complicates the attempt to improve the laser-action properties of the syn-bimanes by substitution at proper positions (R_1 or R_2) of the molecule.

With the exception of halogen substituents, a bimane directly attached to an electron-rich auxochrome [i.e., -OH, -OCH$_3$, -NH$_2$, -NHR$_1$, -N(R$_1$)$_2$], remains unknown even though many proposed synthesis pathways have been extensively investigated. Although the phenyl group is not an auxochrome in the classical sense (has absorbance in the near UV), it acts as an electron-donating substituent.

We collected spectroscopic data on syn-(methyl,chloro) bimane [20,25] to compare these data with those on syn-(phenyl, chloro) bimane, the compound discussed in the following paragraph. As expected, this syn-bimane shows strong resemblance to that of the syn-(methyl, hydrogen) bimane.

From Fig. 11, it is apparent that substitution of two phenyl groups in the R_2 position has a strong effect on the T-T absorption spectrum. Although the lowest energy S-S absorption band that was seen in syn-(methyl,chloro) bimane at 365 nm shifted only to 369 nm for the diphenylbimane, the positively polarized T-T absorption band shifted from 496 to about 600 nm. It should be stressed that substituting along the short axis resulted in a rather large red shift of the positively polarized T-T absorption band. This implies that not only the S-S absorption band at about 360 nm in the syn-bimanes, in which the excitation took place, was polarized along the short axis (i.e., the N-N axis of the molecule), but also the T-T absorption band originally located at 496 nm. The T-T absorption band polarized along the long axis and originally located at about 430 nm also behaves as expected. After substitution along the short axis (R_2) of the molecule, its spectral location was slightly shifted to about 455 nm.

In Fig. 12, we present the spectra of syn-(methyl,phenyl) bimane. Surprisingly, the short axis polarized S-S absorption band was red shifted by a long axis substitution to about 405 nm. In addition, the T-T absorption band polarized along the short axis was shifted to 520 nm. These effects are partially attributed to conjugation between a carbonyl and a phenyl group. This T-T absorption spectrum is somewhat broad, a result to be expected when the phenyl groups are not coplanar with the bimane structure. As expected, the T-T absorption band polarized along the long axis was red shifted from its original position at about 420 nm and became buried under the positive polarized T-T absorption band. According to Fig. 12, it is still recognizable as a shoulder at about 475 nm.

In summary, the presence of two differently polarized T-T transitions in the spectral region of fluorescence in the syn-bimanes complicates the effect of substitution on these two transitions. R_2 (short-axis) substitution by an electron-donating group will move the T-T absorption band polarized along the short axis and originally located at about 480 nm

to longer wavelengths, while the S-S absorption band at 360 nm and polarized along the short axis will not be greatly affected. This implies that the fluorescence intensity maximum will only be shifted slightly. Even a large solvato-chromic effect will result in strong T-T absorption coinciding with the fluorescence spectral region.

R_1 (long axis) substitution with an interacting group appears more promising. Although the T-T absorption band polarized along the short axis is slightly red shifted and broadened by long-axis substitution with two phenyl groups, the small red shift and broadening might not occur when other groups with different electronic properties are used.

By simply inserting an analyzer ∧ (a polarizer) within the path of the monitoring light, one obtains, without any additional experimental effort, additional, very valuable spectroscopic data. Without the $P(\lambda)$ curve on top of the T-T absorption spectra shown in Figs. 9 to 11, one would not be able to furnish an explanation of the somewhat complicated substitution effects on the S-S and T-T absorption spectra of the syn-bimanes studied.

ACKNOWLEDGMENT

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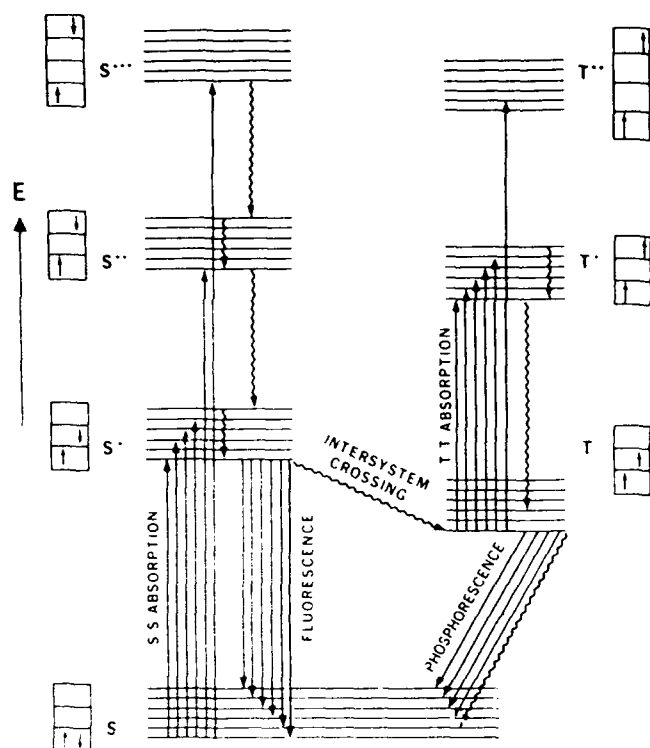25. T. G. Pavlopoulos, J. H. Boyer, C. M. Lau, I. R. Politzer, Spectrochim. Acta 45A, 1057 (1989).

Fig. 1. Energy level diagram of an organic molecule. Small arrows in boxes indicate spin orientation of electrons in outer orbitals.
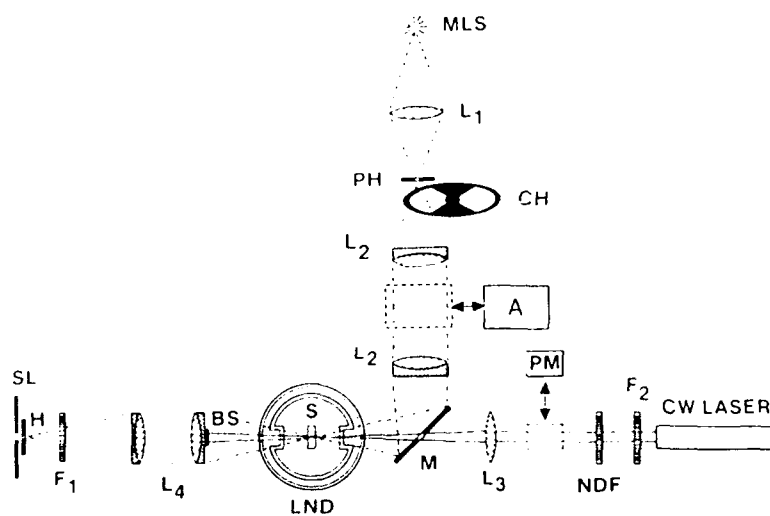

Fig. 2. Experimental arrangement. MLS, monitoring light source; L_1 - L_4, lenses; PH, pinhole; CH, mechanical chopper; SL, monochromator slit; H, small hole in dovetail plate; BS, laser beam stop; F_1, filter that absorbs the laser light; LND, liquid nitrogen dewar; S, sample; M, mirror with hole in center; PM, power meter; NDF, neutral density filter; F_2, filter that passes laser light only; A, analyzer.
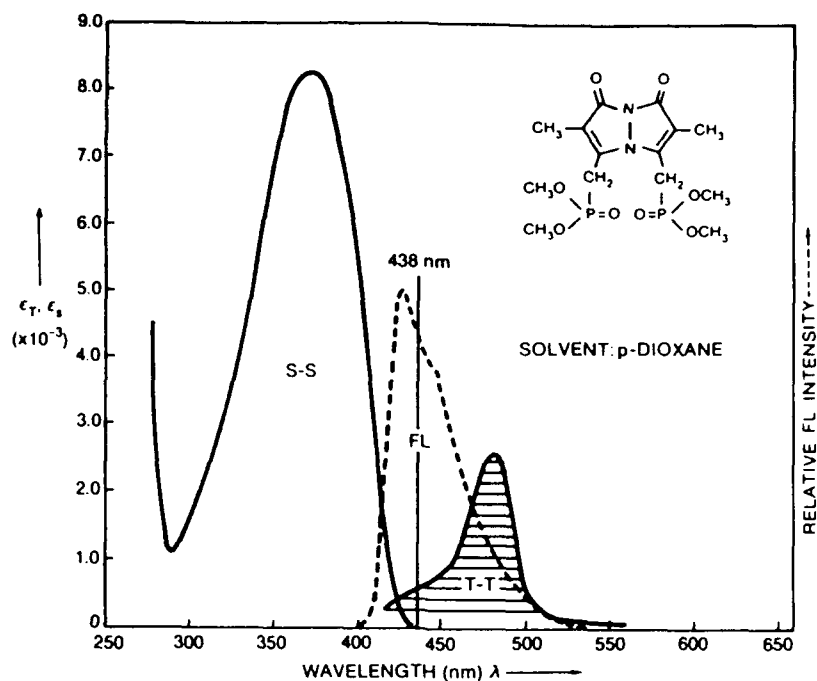
Fig. 3. Absorption (S-S and T-T), fluorescence (FL), and the center of broadband laser activity at 438 nm for syn-(dimethoxyphosphinylmethyl. methyl) bimane in p-dioxane. The T-T absorption spectrum was recorded at $77°K$, employing a $2\times10^{-4}M$ solution of 2-methyltetrahydrofuran. The S-S an FL $(1\times10^{-3}$ M) spectra were recorded with p-dioxane as solvent.
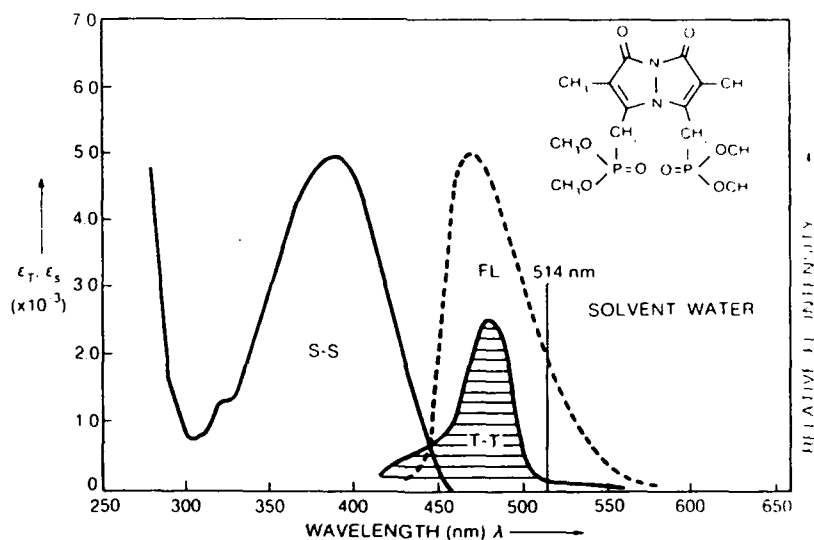
Fig. 4. Absorption (S-S and T-T), fluorescence (FL), and the center of broad-band laser activity at 514 nm for syn-(dimethoxyphosphinylmethyl, methyl)bimane. The T-T absorption spectrum was recorded at $77°K$, employing a 2×10^{-4} molar solution of 2-methyltetrahydrofuran. The S-S and Fl (1×10^{-3}) spectra were recorded with water as a solvent.
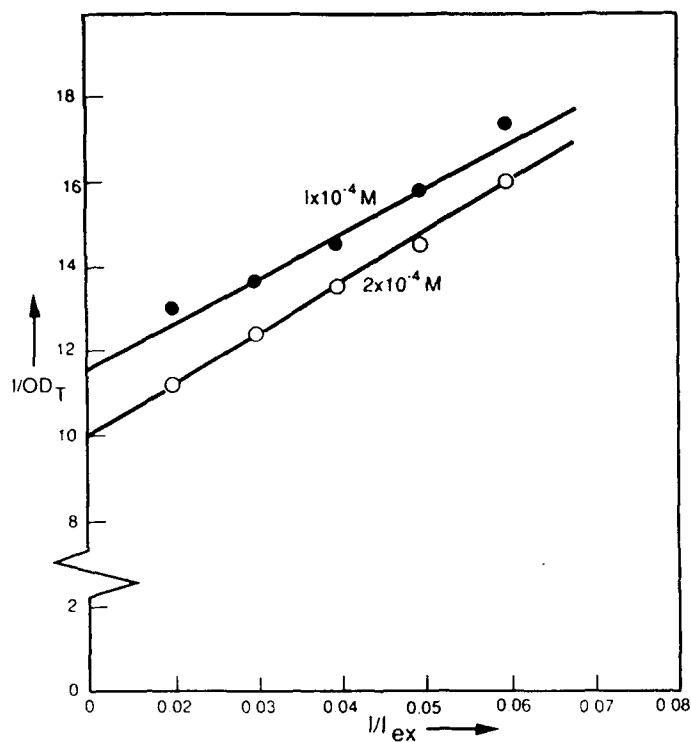
Fig. 5. A plot of $1/OD_T$ vs $1/I_{ex}$ to obtain $1/OD_T^\infty$ by extrapolation of syn-(dimethoxy-phosphinylmethyl,methyl)-bimane dissolved in 2-methyltetrahydrofuran. The OD_T values were recorded at the T-T absorption maximum at 480 nm.
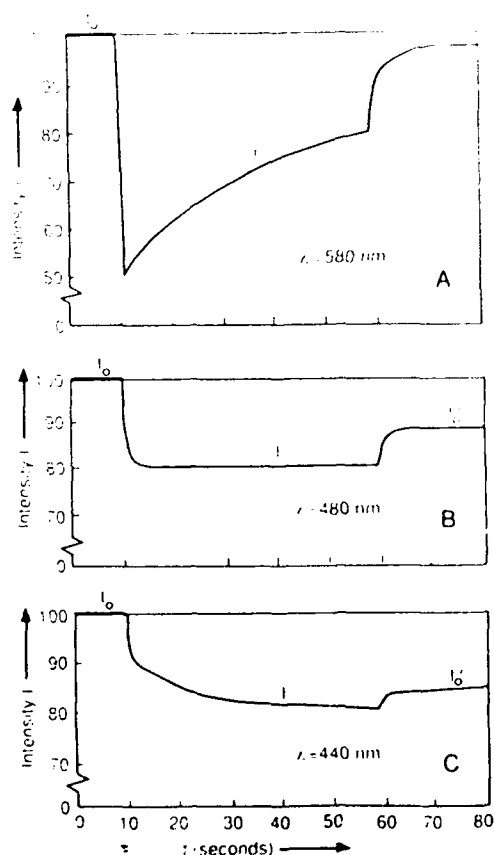

Fig. 6. Three typical monitoring light intensity curves as function of time t and wavelengths λ (A = 580 nm, B = 480 nm, and C = 440 nm). Starting with I_o = 100 (relative light intensity), the sample containing a 1×10^{-4} molar solution of Coumarin 120 dissolved in a mixture of n-butanol/iso-pentane ratio 3:7 is excited with laser light after t = 10 s. After 50 s, the excitation light is turned off. The excited-state molecules N_T then decay exponentionally back to the ground (singlet) state N_S. When N_T = 0, the monitoring light intensity reads I_o'.
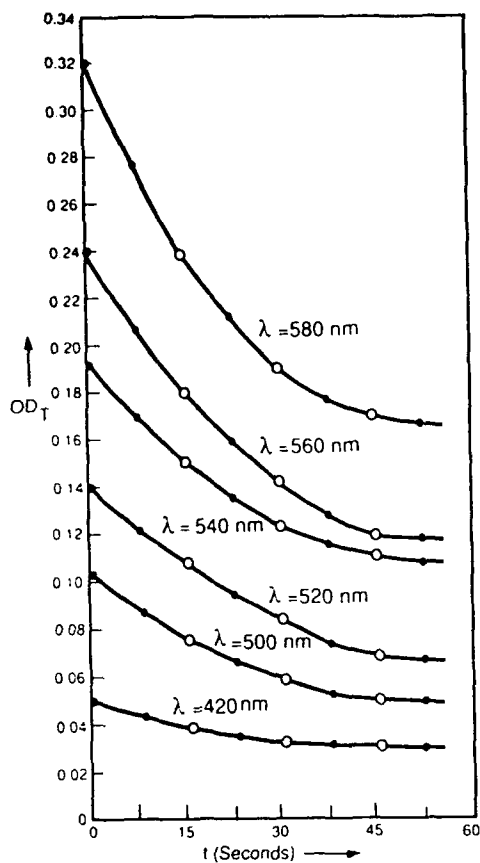
Fig. 7. Triplet optical densities OD_T values (corrected for photodecomposition) recorded after t_1 = 15-; t_2 = 30-; and t_3 = 45-s intervals, measured at different wavelengths. They are presented as circles. The constants A_1, A_2, and A_3 were calculated and used to obtain t = 0-; 7.5-; 22.5-; 37.5-; and 52.5 s. The calculated OD_T values at these time intervals are presented as points. OD_T (t=0) = A_1.
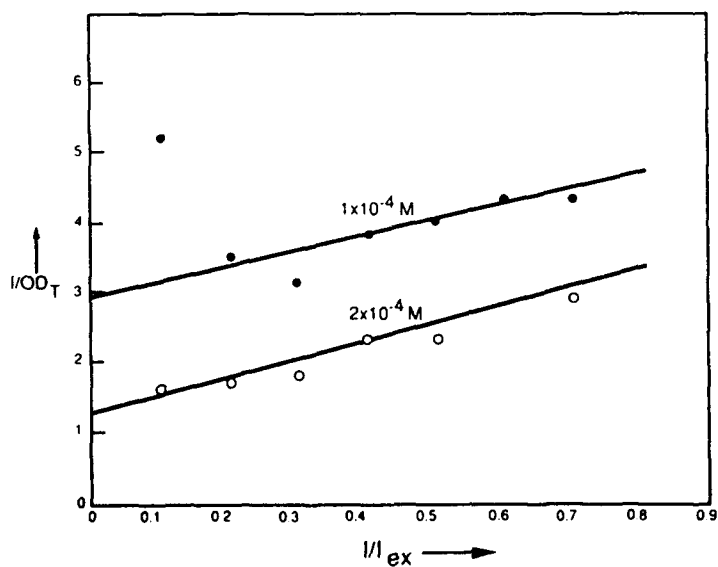

Fig. 8. Using the A_1 (= OD_T) at t = 0 values that were calculated with the aid of Eq. (11), were measured at the maximum of T-T absorption at 580 nm. These values are used to plot $1/OD_T$ vs $1/I_{ex}$ to obtain $1/OD_T^\infty$ by extrapolation. As glassy solvent, the mixture n-butanol/iso-pentane ratio 3:7 was used.
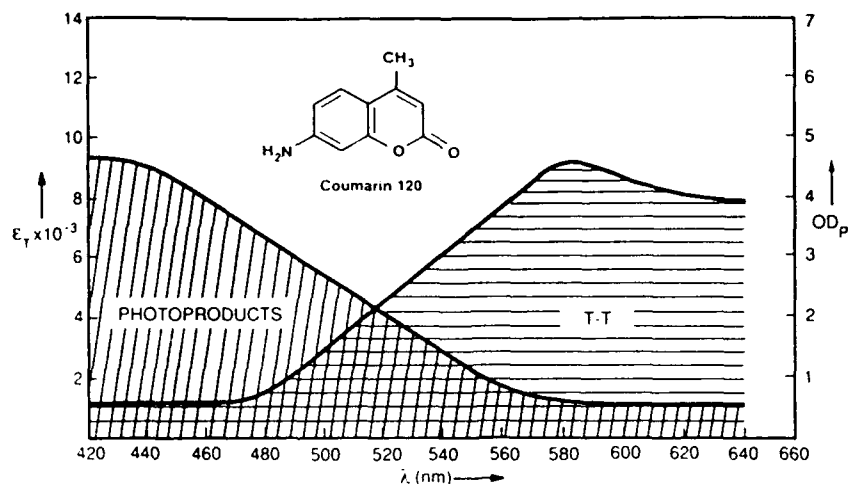
Fig. 9. T-T absorption spectrum presented as ϵ_T as function of wavelength λ and absorption spectrum of the photodecomposition products presented as OD_p as function of wavelength λ of Coumarin 120.
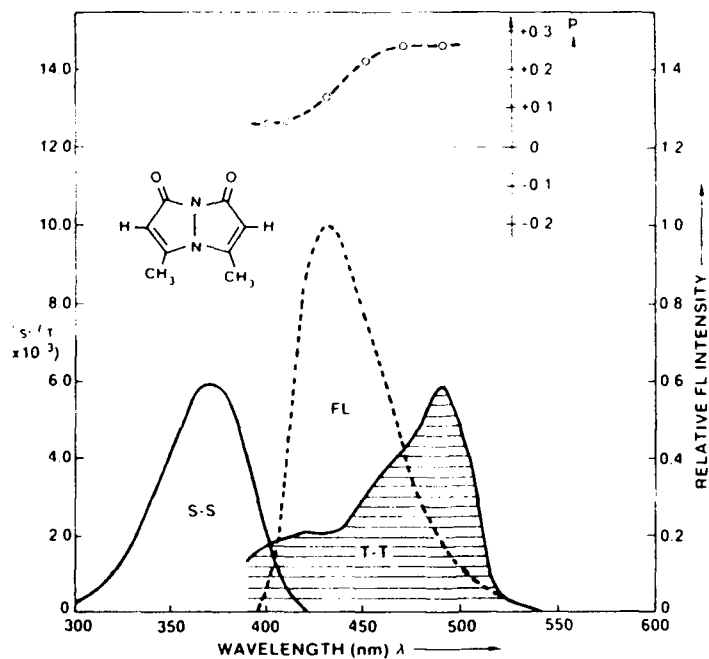

Fig. 10. Electronic transition of syn-(CH_3, H)bimane. The S-S absorption was measured by using a 1.3×10^{-4} molar solution in water; the T-T absorption and polarization were measured at 77°K by using a 2×10^{-4} molar solution in 2-methyltetrahydrofuran; and the fluorescence spectrum was recorded by using a 6.5×10^{-5} molar solution in water.
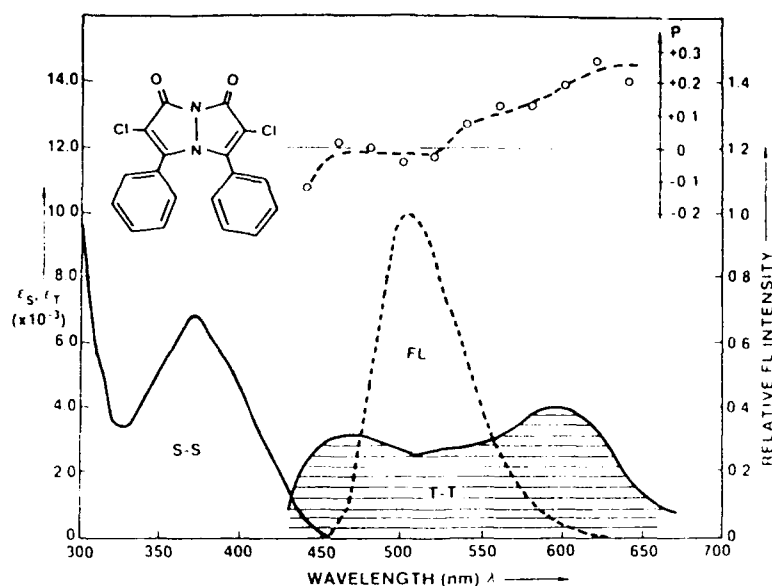
Fig. 11. Electronic transitions of syn-$(C_6H_5$, Cl)bimane. The S-S absorption was measured by using a 5×10^{-5} molar solution in hexafluoroisopropanol; the T-T absorption and polarization were measured at 77°K by using a 5×10^{-5} molar solution in 2-methyltetrahydrofuran; the fluorescence spectrum Fl was recorded by using a 1×10^{-4} molar solution in hexafluoroisopropanol.
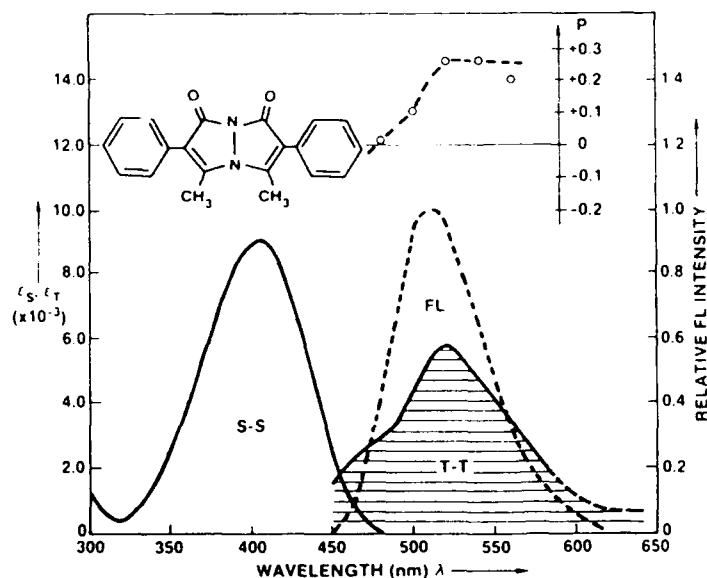

Fig. 12. Electronic transitions of syn-(CH_3,C_6H_5) bimane. The S-S absorption was measured by using a 1.05×10^{-5} molar solution in trifluoroethanol; the T-T absorption and polarization were measured at 77°K by using a 1.1×10^{-4} molar solution in 2-methyltetrahydrofuran; the fluorescence spectrum Fl was recorded by using a 5×10^{-4} molar solution in trifluoroethanol.